Towards Self-Healing Organic Electronics

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Summary

The European Union, U.S.A. and various other countries are implementing policies to reduce greenhouse gas emissions. The reduction of energy consumption by lighting, and increased energy production by renewable energy sources are two of these policies. When considering lighting, a significant amount of greenhouse gas emission follows from the use of inefficient incandescent light sources (5% efficiency). These light bulbs need to be replaced with more efficient types of lighting in order to reduce power consumption. A highly promising alternative to incandescent light sources are the light-emitting diodes (LEDs).

LEDs are based on crystalline semiconductor technology. They have a small emitting surface, are very efficient ($\sim$ 30%), have low power consumption (100 lm/W) and do not have the drawbacks of other alternative light sources such as compact fluorescent lights. That is, they do not exhibit decreased performance at low operating temperatures, or reduced life-time when turned on for a few minutes at a time. LEDs are at the moment the most worthwhile alternative to incandescent light sources due to their efficiency and low cost of ownership.

If one considers renewable energy sources, widespread adoption of solar energy is a promising solution to reduce greenhouse gasses. "Classic" solar cells are, like LEDs, based on semiconductor technology. For inorganic solar cells, record light to-power-conversion efficiencies over 40% have been achieved. Unfortunately, fabrication costs of solar cells are relatively high due to the need to purify silicon, as well as the relatively low production throughput.

LEDs and solar cells based on organic semiconductor materials are promising supplementary technologies for "classic" crystalline semiconductors. The biggest advantages of using organic materials to fabricate organic light-emitting diodes (OLEDs, > 100 lm/W at 1000 cd/m2 efficacy) and organic solar cells (OSCs, 10 % light to power conversion efficiency) are chemical tenability and easy processing. These factors allow organic semiconductors to be fabricated at low temperature, using wet processing methods. As a result, production costs of OLEDs and OSCs can be decreased significantly since high-throughput manufacturing methods from the printing industry can be employed.

OLEDs and OSCs are composed of one or more thin (< 100 nm) stacked organic layers sandwiched between an anode and cathode. However, as large areas need to be covered with very thin organic layers, there are significant challenges that need to be overcome during deposition of the organic materials. Particles and/or inhomogeneities on the sub-

strate during deposition of the thin layers can easily result in small areas where the bottom electrode is not covered by the organic materials. Subsequent deposition of the top electrode then easily results in short-circuits (shunts) between the electrodes enclosing the organic layer stack. Such short-circuits give rise to catastrophic device failure, lowered production yield, and increased production costs. They therefore need to be prevented effectively in order to facilitate large scale, low-cost, production of OLEDs and OSCs. In this thesis additional processing methods, steps and repair-procedures were investigated that prevent short-circuits and other types of defects in organic electronics.

In chapter 4 we proposed a highly successful method to prevent microscopic shunts in OLEDs. The method was based on immersion of an OLED precursor (ITO/PEDOT:PSS/ light-emitting polymer), prior to cathode deposition, in a solution of sodium hypochlorite. Sodium hypochlorite is an oxidizing agent known to over-oxidize and concomitantly demolish the conductive properties of PEDOT:PSS. We studied the reaction kinetics between hypochlorite and PEDOT:PSS in chapter 3, and found that for low (<0.05%) $NaClO_{(aq)}$ concentrations the over-oxidation process is reaction-limited, while diffusion-limited for higher concentrations. The decrease in conductivity of a layer of PEDOT:PSS, as function of treatment time and hypochlorite concentration, could successfully be modeled using general effective medium theory, of which the fitting parameters suggested a filamentary morphology of PEDOT domains in a PSS matrix. The conductivity of PEDOT:PSS was completely annihilated after a treatment of 30 seconds in 5 % hypochlorite, leaving a residual layer of over-oxidized, insulating, 'PEDOT:PSS'.

Immersion of a light-emitting polymer (LEP) in hypochlorite, for the same process time, had no significant effect on the photo-luminescent properties of the polymer, as evident from the results in chapter 4. Therefore, a process window was obtained that would allow the deactivation of locally uncovered PEDOT:PSS in pinholes and other defected areas, while leaving the luminescent properties of the LEP intact. The procedure was tested in chapter 4 on OLEDs with artificially fabricated microscopic pinholes, and pristine, not defected devices. Hypochlorite treated OLEDs showed reduced parasitic currents, a decrease in the occurrence of bright spots, and equal lifetime compared to untreated (reference) devices. It was therefore concluded that the hypochlorite treatment proves a highly effective method to prevent short-circuits in OLEDs.

The treatment method from chapter 4, for OLEDs, was applied to conventional P3HT:PCBM-based organic solar cells in chapter 5. Based on results from contact angle measurements, it was found that polythiophene in the P3HT :PCBM blend was oxidized when exposed to hypochlorite. Therefore, total immersion of the OSC precursor in hypochlorite was deemed unsuitable, and uncovered areas of PEDOT:PSS had to be treated locally. Upon local treatment, macroscopic holes in the photoactive layer, comprising 5% of the active device area, could successfully be deactivated by locally exposing the underlying PEDOT:PSS to hypochlorite. Device performance for OSCs with LiF/Al or Ba/Al cathodes was found to be equal for pristine (undefected) and defected, but hypochlorite-treated, organic solar cells.

We noted however that from a processing point of view, it is less than optimal when defects in the photoactive layer need to be detected prior to application of hypochlorite. We therefore proceeded in chapter 6 with investigating a different method to deactivate shunts in OSCs. A simple equivalent circuit model involving a diode, a series

resistance, and a parallel shunt resistance was used to predict that short-circuits in conventional OSCs have little to no effect on device performance as long as their resistance is higher than 1000 Ohms. By studying charge transport across PEDOT:PSS-lithium fluoride/aluminum (LiF/Al) shunting junctions we showed that this prerequisite is already met when a sufficiently thick (> 1.5 nm) LiF layer is applied. We demonstrated that this remarkable shunt-resilience stems from the formation of a significant charge transport barrier at the PEDOT:PSS-LiF/Al interface, in which charge transport exhibits Poole-Frenkel-like behavior. We validated our predictions of self-healing shunts by fabricating OSCs with deliberately severed photoactive layers and found an excellent agreement between the calculated and experimental current-voltage characteristics. The resilience of OSCs against processing imperfections or damage to the photoactive layer is therefore considerably enhanced by applying a cathode with a relatively thick LiF layer, as it allows the formation of a self-healing current barrier at the anode/cathode interface.

Finally we showed in chapter 7 that fractures in silver grid lines, commonly used in large area organic electronics, could also be self-repaired. The repair procedure was based on the formation of dendritic metal structures that connect both anode and cathode side of the crack, using the process of electro-deposition. The organic anode is typically in direct contact with the silver grid, and can function as an appropriate medium for ion migration. Dendritic silver growth within the fracture could therefore be incited upon application of a moderate DC voltage across the crack. The formed dendrites decreased the gap resistance by one order of magnitude. Subsequently, another three orders of magnitude were gained upon sintering of the dendrites using a high voltage pulse, yielding restored conductance levels nearly within one order of magnitude difference from native track conductivity.